

**Induced Lanthanide Circularly Polarized Luminescence as a Probe of Protein Fibrils**

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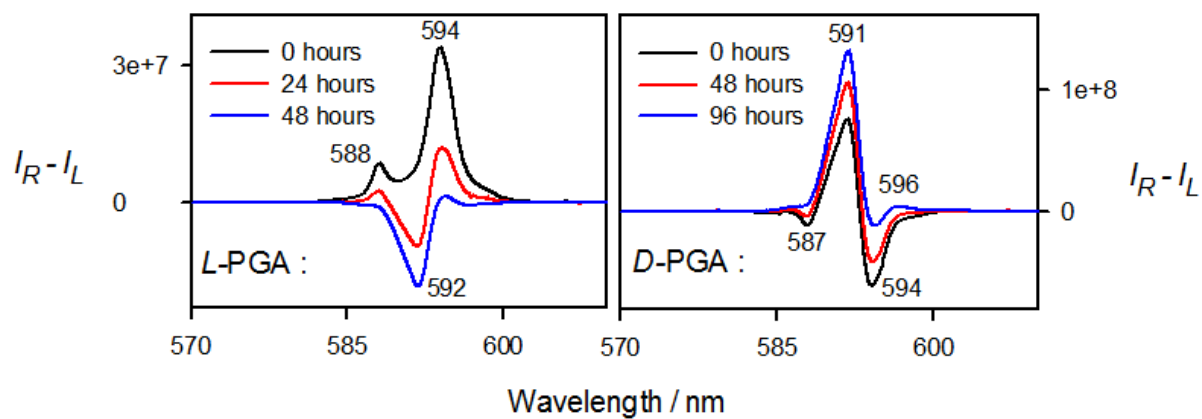
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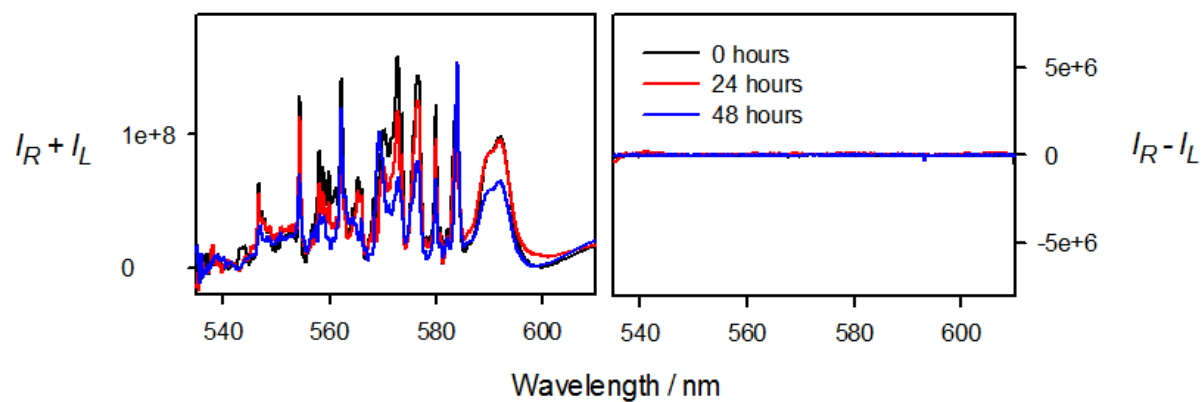
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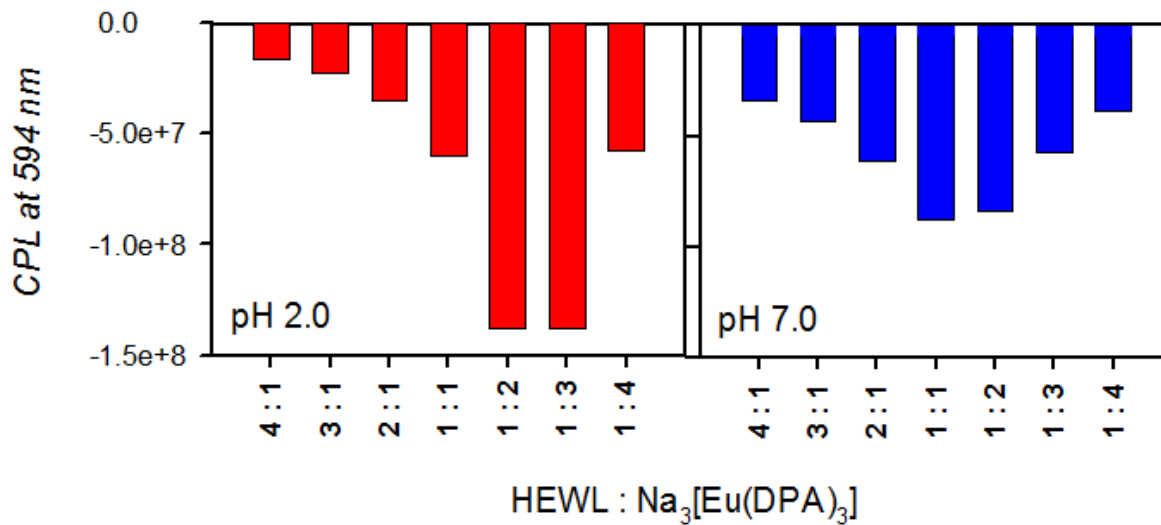


**Figure S1.** Comparison of time dependence of  $\text{EuCl}_3$  CPL spectra induced by PLGA and PDGA fibrils.

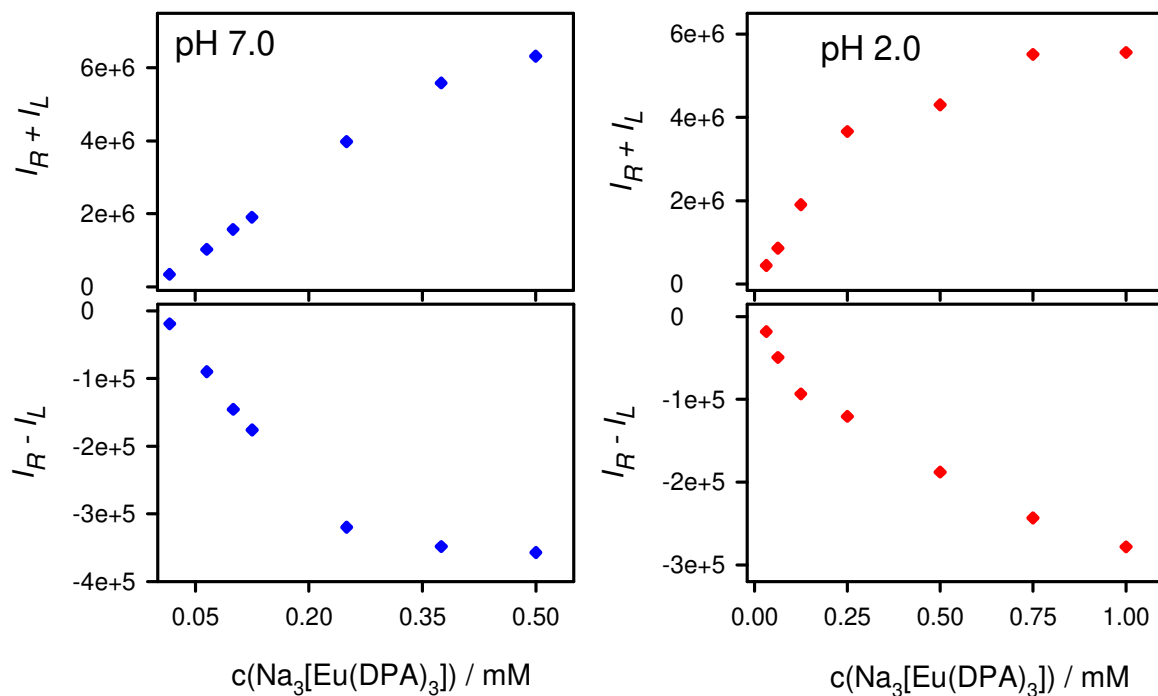


**Figure S2.**  $\text{EuCl}_3$  TL/Raman and CPL/ROA spectra in the presence of growing HEWL fibrils.

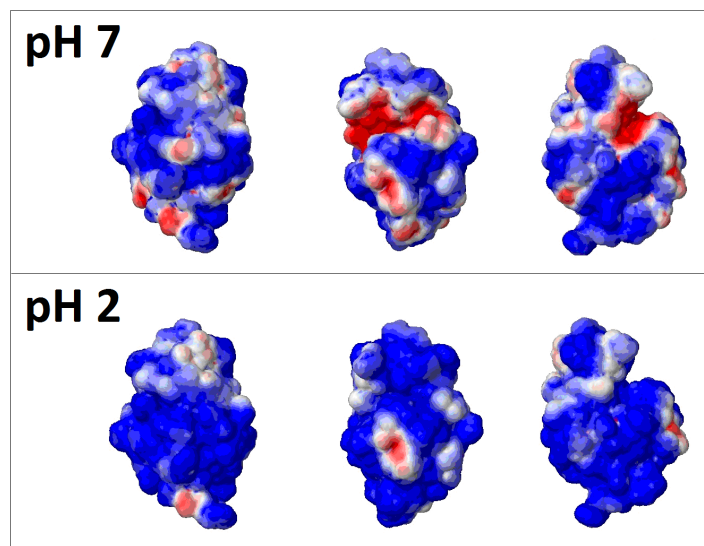
A)



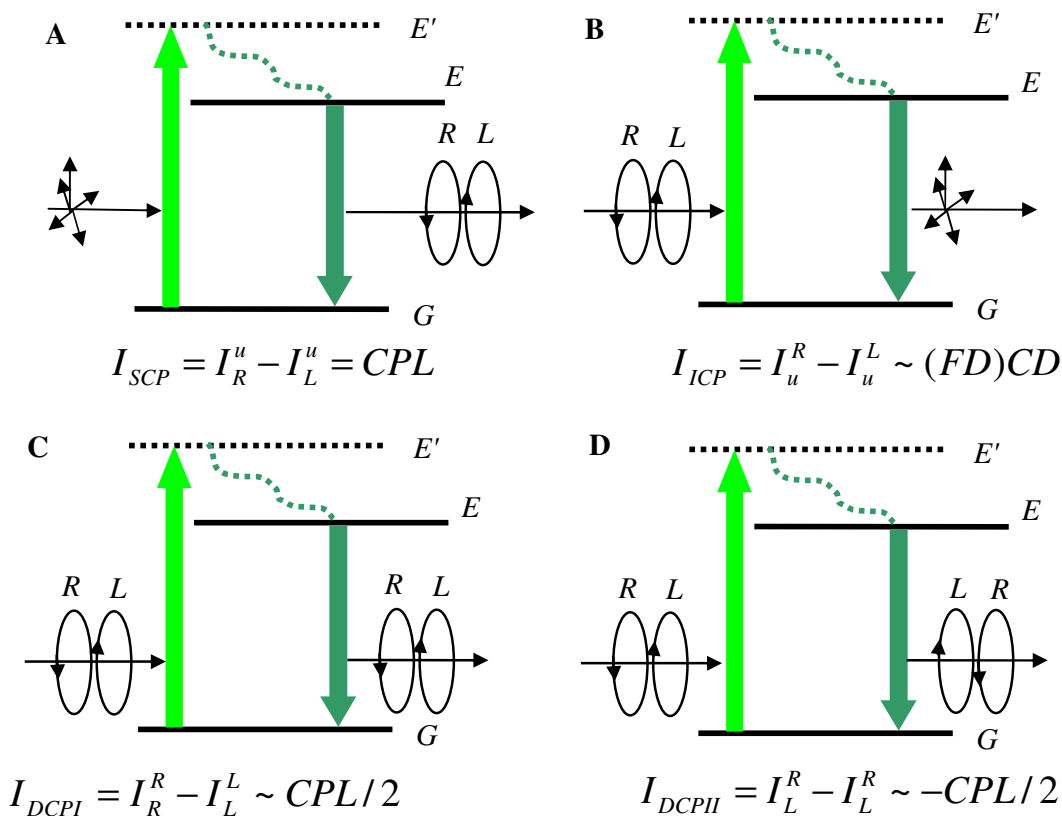
B)



**Figure S3.** (A) Job's plots of CPL for HEWL titrated by  $\text{Na}_3[\text{Eu}(\text{DPA})_3]$ , for two pH values and (B) total and circularly polarized luminescence at 594 nm as dependent on the complex concentration. For (A), sum of molar concentrations of HEWL and  $\text{Na}_3[\text{Eu}(\text{DPA})_3]$  was 0.5 mM, for (B) concentration of HEWL was 0.25 mM.



**Figure S4.** Electrostatic potential surface map of HEWL at pH 7<sup>1</sup> (top) and pH 2<sup>2</sup> (bottom). As calculation of protonation states of aminoacids by PROPKA 3.0<sup>3,4</sup> showed, HEWL acquires total net charge of +8 at pH 7. At pH 2, total net charge of the protein is increased to +18. EPS map of HEWL was obtained by online visualization tool introduced in CHARMM-GUI.<sup>5,6,7</sup>



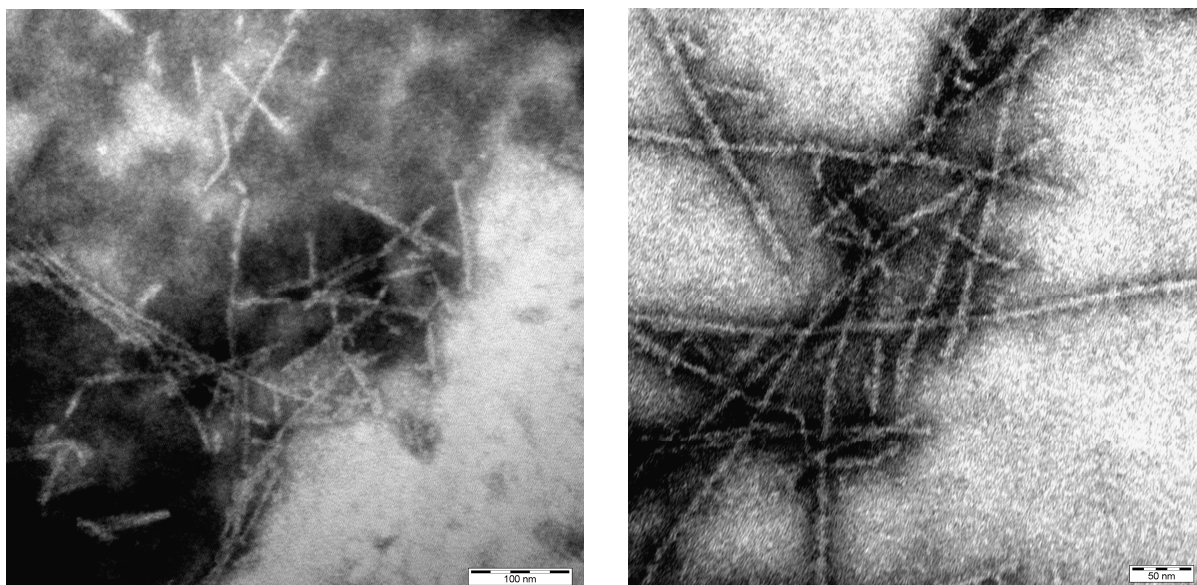
**Figure S5.** Overview of the ROA instrument polarization modes. Meaning of the polarization modes:

**A:** SCP, scattered circular polarization, sample is irradiated with unpolarized light and difference in right and left circular polarization is detected, which provides circular polarized luminescence.

**B:** ICP, incident circular polarization, sample is irradiated by right or left circular polarized light, and difference intensity of outgoing unpolarized light is measured, corresponding to (fluorescence-detected) circular dichroism of the  $G \rightarrow E'$  transition (at the 532 nm laser excitation).

**C:** DCP<sub>I</sub>, dual circular polarization of the first kind, intensity of outgoing right circular polarization under the same excitation polarization minus outgoing intensity with opposite polarizations, a function of circular dichroism ( $G \rightarrow E'$ ), energy transfer ( $E' \rightarrow E$ ) and CPL ( $E \rightarrow G$ ), approximately equal to  $CPL/2$  if CPL dominates.

**D:** DCP<sub>II</sub>, DCP of the second kind, analogous to DCP<sub>I</sub> (see the formulas, the upper index denotes incident and the lower one scattered polarization), equal to  $-CPL/2$  if CPL dominates.



**Figure S6.** TEM images of PLGA (left,  $2.5 \times 10^5$  magnification) and HEWL (right,  $3 \times 10^5$  magnification) fibrils.

## References

1. 2HUB pH 7.5, DOI: 10.2210/pdb2HUB/pdb
2. 3WUN pH 3, DOI: 10.2210/pdb3WUN/pdb
3. S ndergaard, C. R.; Olsson, M. H. M.; Rostkowski, M.; Jensen, J. H., Improved Treatment of Ligands and Coupling Effects in Empirical Calculation and Rationalization of pKa Values. *J. Chem. Theory Comput.* **2011**, 7(7), 2284-2295.
4. Olsson, M. H. M.; S ndergaard, C. R.; Rostkowski, M.; Jensen, J. H., PROPKA3: consistent treatment of internal and surface residues in empirical pKa predictions. *J. Chem. Theory Comput.* **2011**, 7(2), 525-537.
5. Jo, S.; Kim, T.; Iyer, V. G.; Im, W., CHARMM-GUI: A Web-based Graphical User Interface for CHARMM. *J. Comput Chem.* **2008**, 29, 1895-1865.
6. Im, W.; Beglov, D.; Roux, B., Continuum Solvation Model: Computation of Electrostatic Forces from Numerical Solutions to the Poisson-Boltzmann Equation. *Comput. Phys. Comm.* **1998**, 111, 59-75.
7. Jo, S.; Vargzas, M.; Vasko-Szedlar, J.; Roux, B.; Im, W., PBEQ-Solver for Online Visualization of Electrostatic Potential of Biomolecules. *Nucl. Acids Res.* **2008**, 36, 270-275.